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Constituents of Pine Heartwood

XXI.* The Structure of Pinobanksin

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Pinobanksin, one of the most common phenolic constituents of pine heartwood, was first isolated from *Pinus Banksiana* by Erdtman [1]. This substance melted at 173—175° and was optically active, $[\alpha]_D^{20}$ + 15° **. Its composition agreed with the formula $C_{15}H_{12}O_5$, and oxidation with alkaline potassium permanganate yielded benzoic acid, thus showing the presence of an unsubstituted phenyl group. Pinocembrin, another common heartwood constituent, has the composition $C_{15}H_{12}O_4$ and is identical with (—)5,7-dihydroxyflavanone [2]. Erdtman assumed that pinobanksin and pinocembrin were structurally related and considered the most probable structure of pinobanksin to be 3,5,7-trihydroxy-flavanone [1], but no further experiments were carried out to prove this assumption.

A few 3-hydroxyflavanones have been found in nature during the last fifteen years, most of them by Japanese chemists. From the seeds of *Alpinia japonica* (Thunb.) Miq., Kimura and Hosi isolated a compound called alpinone, m. p. 178°, $[\alpha]_D^{20}$ + 79.1° (in pyridine), which they claimed to be 2-methyl-3,5-dihydroxy-7-methoxyflavanone [3, 4]. Fustin, a constituent of the wood from some *Rhus* species, was isolated as early as 1886 [5]. Its structure was elucidated by Oyamada in 1939.[6] It is a 3,7,3′,4′-tetrahydroxyflavanone, m. p. 216—218°. (The optical activity — if any — of fustin does not seem to have been determined.) Another 3-hydroxyflavanone, called ampelopsin, was isolated from the leaves of *Ampelopsis meliaefolia* Kudo. It has been shown to be a 3,5,7,3′,4′,5′-hexahydroxyflavanone, m. p. 245—246°, and is optically inactive [7]. It should be noted that both fustin and ampelopsin are accompanied by the corresponding flavonol, fisetin and myricetin, respectively. Two other

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** The value + 1.5° given in Erdtman's paper is due to a misprint.

3-hydroxyflavanones were isolated by Pew [8], namely 3,5,7,3′,4′-pentahydroxyflavanone (taxifolin) from the heartwood and bark of *Pseudotsuga taxifolia* Britt. (Douglas-fir), m. p. 240—242°, $[\alpha]_D^{20}$ + 46° (in 50 % acetone)*, and 3,5,7,4′-tetrahydroxyflavanone, m. p. 237—241°, $[\alpha]_D^{20}$ + 45° (in 50 % acetone) from the heartwoods of *Notofagus dombeyi* Bl. (coigue) and of *Prunus serotina* Ehrh. The latter structure has also been ascribed to katsuranin, m. p. 224—225°, which has been isolated from the wood of *Cercidiphyllum japonicum* Sieb. et Zucc.[9]

In the course of the present author's investigations, pinobanksin has been isolated from the heartwood of several pine species [10]. By paper partition chromatography [11], it has been shown to be present in most pines.

The separation of pinobanksin from heartwood extracts is facilitated by its precipitation as an insoluble sodium salt with saturated sodium carbonate solution [1]. The pinobanksin is then liberated by acidification of the salt and purified by recrystallisation from toluene or from methanol-water. From toluene, it crystallises in large thick, colourless needles. After drying, the m.p.is 177—178°** and $[\alpha]_D^{20}$ +14.4° (in methanol). The loss in weight on drying at 110° corresponds to the composition 2 $C_{15}H_{12}O_5 \cdot C_7H_8$. Pinobanksin gives an orange-red colour when reduced with magnesium or zinc and hydrochloric acid. Pinocembrin gives an orange colour with magnesium but no colour with zinc, which confirms the statement by Pew[8] that the zinc colour reaction is specific to 3-hydroxyflavanones. (Flavanones containing hydroxyl groups on the side phenyl group give much deeper colours when reduced.)

Pinobanksin shows great resistance to racemisation. Treatment with 1 % sodium hydroxide for 43 hours at room temperature only depressed the specific rotation from + 14° to + 11°. (Pinocembrin is racemised completely under these conditions.) Boiling with alcoholic hydrochloric acid for one and a half hours did not change the rotation at all. Pew reports total racemisation of taxifolin after similar treatment [8]. When pinobanksin was treated with 15 % sodium hydroxide for seven days, a crystalline product, melting gradually at 180—200°, and having $[\alpha]_D^{20}$ + 5.5°, was obtained. Some decomposition of the molecule had evidently taken place in this experiment.

Pinobanksin gives a tribenzoate, m. p. 172—173°. Methylation with diazomethane yields a monomethyl ether, $C_{16}H_{14}O_5$ (II), m. p. 181—182°, $[\alpha]_D^{20}$—19° (in chloroform). A dimethyl ether, $C_{17}H_{16}O_5$ (III), can be prepared from the monomethyl ether by further methylation with one mole of dimethyl

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* In absolute ethanol, taxifolin has $[\alpha]_D^{20}$ + 13°, which lies close to the rotation of pinobanksin in methanol.

** All melting points uncorrected.

sulphate and anhydrous potassium carbonate in acetone solution. This method has been frequently employed by Seshadri and co-workers for the methylation of flavones and similar compounds [12]. The dimethyl ether can also be prepared by direct methylation of pinobanksin, but the overall yield is lower than for the two-step methylation. The dimethyl ether melts at 133—134° and has $[\alpha]_D^{20}$—31° (in chloroform). It is insoluble in dilute alkali and gives no colour with ferric chloride.

The structure of pinobanksin is shown by the catalytic dehydrogenation to the corresponding flavonol, galangin (IV). The dehydrogenation is carried out at 180° with a palladium-charcoal catalyst employing cinnamic acid as a hydrogen acceptor. The same method was used by Kotake and Kubota for the dehydrogenation of ampelopsin pentamethyl ether to the corresponding myricetin derivative [7].

Dehydrogenation by air, which has been successfully applied to taxifolin [8], failed with pinobanksin. The dimethyl ether can also be dehydrogenated by palladium-cinnamic acid to galangin-5,7-dimethyl ether (V). A spontaneous dehydrogenation takes place, when pinobanksin is methylated with an excess of dimethyl sulphate in acetone solution. Instead of pinobanksin trimethyl ether, galangin trimethyl ether (VI) is obtained in poor yield. A similar dehydrogenation during methylation has been observed with fustin [6].

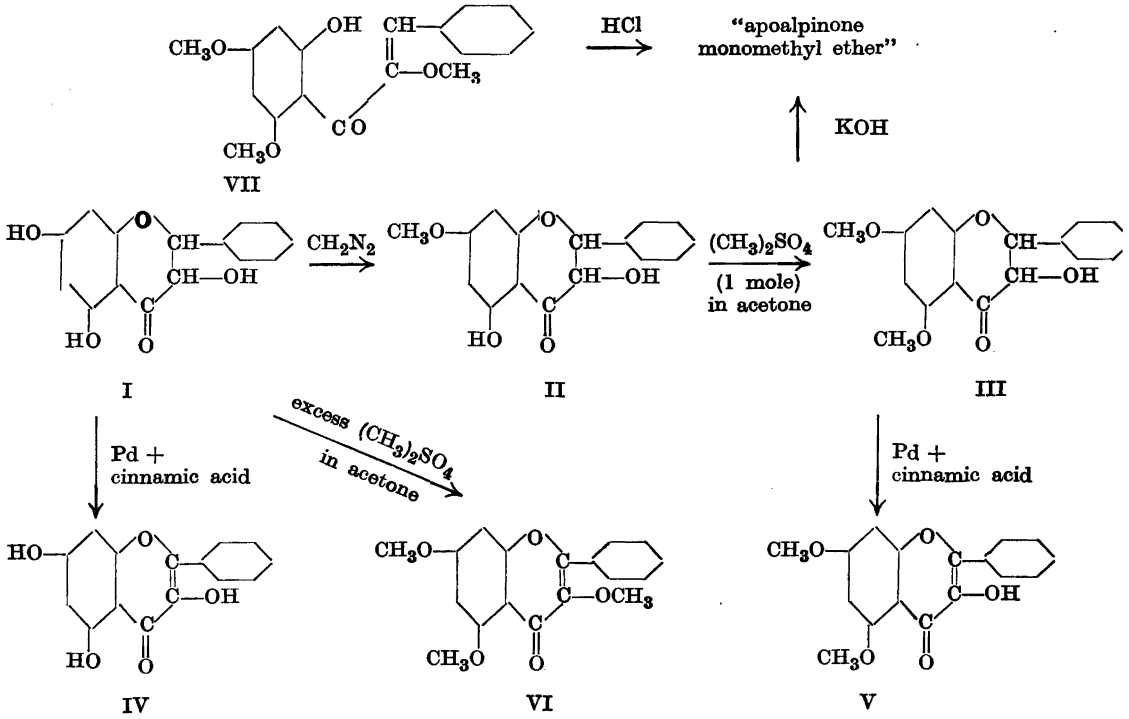
The methoxyl group in pinobanksin monomethyl ether certainly occupies the 7-position, since the hydroxyl group in the 5-position is much more difficult to methylate because of chelation with the carbonyl group [15]. It is to be noted that the isolation of a substance having the structure (II), apoalpinone, has been reported by Kimura and Hosi [3, 4]. It was obtained by treatment of alpinone with alkali and melted at 148°. Probably this compound differs from pinobanksin monomethyl ether only in the configuration at carbon atoms 2 and 3.

When pinobanksin dimethyl ether is boiled with alcoholic potassium hydroxide for a few minutes, it is rearranged to an optically inactive compound, m. p. 170—171°, which has the same composition as the optically active compound. This compound is identical with "apoalpinone monomethyl ether", which was first prepared by Kimura [13] by boiling 2'-hydroxy-4',6', α-trimethoxychalkone (VII) with alcoholic hydrochloric acid. Repetition of Kimura's synthesis (starting from 2-hydroxy-4,6, ω-trimethoxyacetophenone prepared according to Row and Seshadri [14]) yielded a colourless substance which melted at 169—170° (Kimura 169°). Its monoacetate (not described before) melted at 112—113°. The identity of the synthetic product with the substance obtained from pinobanksin dimethyl ether was established by the mixed melting points of the two substances themselves and their acetates. According to Kimura, "apoalpinone monomethyl ether" should be 3-hydroxy-5,

7-dimethoxyflavanone and thus should be a stereisomer of pinobanksin dimethyl ether. There are, however, some differences in the chemical behaviour of the two substances which cannot possibly be due only to different configuration at carbon atoms 2 and 3. For example, pinobanksin dimethyl ether gives an orange colour when reduced with magnesium-hydrochloric acid as does pinobanksin itself, while "apoalpinone monomethyl ether" gives no colour reaction at all. Furthermore, the latter substance dissolves readily in 2 *N* sodium hydroxide in the cold (and to a smaller extent even in more dilute alkali). Pinobanksin dimethyl ether is insoluble under the same conditions as would be expected from its structure. An attempt to dehydrogenate "apoalpinone monomethyl ether" to galangin 5,7-dimethyl ether failed completely. Thus, "apoalpinone monomethyl ether", apparently, is not a flavanone, and its formation by rearrangement of pinobanksin dimethyl ether will not be considered here as a proof of the structure of this substance.

Kimura's "apoalpinone monomethyl ether" has not been obtained by methylation of the apoalpinone mentioned above, but both substances yield the same product, "apoalpinone dimethyl ether", m. p. 108—109°, on exhaustive methylation [4, 13]. This substance is claimed to be 3,5,7-trimethoxyflavanone, but no rigorous proof of the structure has been given.

The following scheme shows the different reactions carried out with pinobanksin (I):



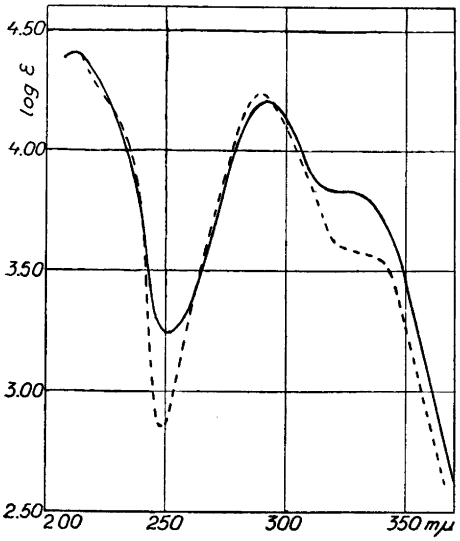


Fig. 1. Ultraviolet light absorption of pinobanksin (———) compared with pinocembrin according to Erdtman [2] (— — —).

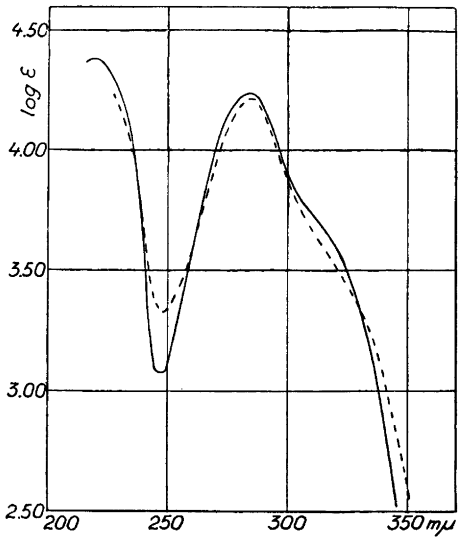


Fig. 2. Ultraviolet light absorption of pinobanksin dimethyl ether (———) compared with 5,7-dimethoxyflavanone according to Skarżyński [16] (— — —).

The ultraviolet absorption curve of pinobanksin (Fig. 1) shows a close resemblance to that of pinocembrin [2]. Pinobanksin dimethyl ether gives an absorption curve which resembles that of 5,7-dimethoxyflavanone [16] (Fig. 2). The absorption maximum lies at 292 mμ for pinobanksin and at 284 mμ for pinobanksin dimethyl ether. The wavelengths for the minima are 251 and 247 mμ respectively. The typical "shelves" for pinobanksin and pinocembrin at 320—330 mμ have been flattened out after methylation.

EXPERIMENTAL

The isolation of pinobanksin from pine heartwood extracts has already been described several times [1, 10]. After repeated recrystallisations from toluene, the pinobanksin forms thick colourless needles. When dried at 110°, they lost 15 % in weight and melted at 177—178° $[\alpha]_D^{20}$ + 14.4° ± 0.3° (methanol, c = 3.0). This rotation was determined in a 1 dm tube, whereas all previous determinations were made in a 0.5 dm micro tube. Colour reactions: Hot nitric acid, brownish-violet; ferric chloride, reddish-violet; diazotised benzidine, cherry red; magnesium-hydrochloric acid as well as zinc-hydrochloric acid, orange red.

$C_{15}H_{12}O_5$ (272.3)	Calc.	C	66.2	H	4.44
	Found	»	66.0	»	4.49

Benzoylation with benzoyl chloride and pyridine yielded the tribenzoate, colourless needles from ethanol, m. p. 172—173°.

$C_{15}H_9O_2$ $(OOCC_6H_5)_3$ (584.6)	Calc.	C_6H_5CO	53.9
	Found	»	52.4

Attempts to racemise pinobanksin

A. In dilute alkali: Pinobanksin (0.4 g, $[\alpha]_D^{20}$ + 14°) was dissolved in 1 % sodium hydroxide (50 ml), and the solution allowed to stand for 43 hours in a hydrogen atmosphere at room temperature. The solution was then acidified with acetic acid, and the pale yellow precipitate separated by filtration, washed with water and dried. M. p. 170—173°, yield 0.3 g. On recrystallisation from toluene, thick colourless needles were obtained. After drying at 110°, they melted at 174—176°. $[\alpha]_D^{20}$ + 11° ± 1° (methanol, c = 2.6).

B. In alcoholic hydrochloric acid: Pinobanksin (0.7 g, from *P. Banksiana*, $[\alpha]_D^{20}$ + 12°) was dissolved in hot ethanol (20 ml). Concentrated hydrochloric acid (10 ml) was added, and the solution boiled for one and a half hours under reflux. It was then diluted with water (100 ml), yielding a colourless crystalline precipitate which was filtered off, washed with water and dried. M. p. 171—174°, yield 0.6 g. After recrystallisation from toluene and drying at 120°, the m. p. was 173—175°. $[\alpha]_D^{20}$ + 12° ± 1° (methanol, c = 6.3).

C. In strong alkali: Pinobanksin (0.1 g, $[\alpha]_D^{20}$ + 12°) was dissolved in 15 % sodium hydroxide (10 ml) and allowed to stand for seven days in a hydrogen atmosphere at ordinary temperature. The yellow solution was then acidified, yielding a colourless precipitate, melting gradually between 150° and 170°. After recrystallisation from toluene and from 50 % acetic acid, the product melted between 180° and 200°, but no pure substance could be isolated. $[\alpha]_D^{20}$ + 5.5° (methanol, c = 2.5). Decomposition or rearrangement of the molecule must have taken place, since the reaction product melted higher than pinobanksin.

Pinobanksin monomethyl ether

Pinobanksin (3.0 g) was dissolved in ether (350 ml) and methylated by addition of a diazomethane solution (about 0.6 g diazomethane in 25 ml of ether). The solution, when left overnight at room temperature, deposited large colourless needles, which were collected. On evaporation of the ether, a second crop of crystals was obtained. Both crystalline fractions (2.3 g) were recrystallised twice from benzene, yielding pure pinobanksin monomethyl ether (1.8 g). Large colourless needles, m. p. 181—182°, $[\alpha]_D^{20}$ — 19° ± 1° (chloroform, c = 2.7). The substance dissolves in hot 1 *N* sodium hydroxide. The alcoholic solution gives a reddish-violet colour with ferric chloride (weaker than for pinobanksin itself) and an orange red colour with diazotised benzidine. Reduction with magnesium-hydrochloric acid gives an orange colour.

$C_{16}H_{14}O_5$ (286.3)	Calc.	C	67.1	H	4.93	OCH_3	10.8
	Found	»	67.0	»	4.93	»	10.9

Pinobanksin dimethyl ether

Pinobanksin monomethyl ether (1.0 g) was boiled with dry acetone (50 ml), dimethyl sulphate (0.37 ml) and freshly ignited potassium carbonate (5 g) on a steam bath, under reflux, for three and a half hours. The potassium carbonate was removed by filtration and washed with hot acetone. The acetone was then evaporated and the residue dissolved in ether. The ether solution (100 ml) was washed with 2 *N* sodium hydroxide (2 × 50 ml) to remove the monomethyl ether which had not reacted. It was then dried over anhydrous sodium sulphate and evaporated to dryness, leaving a yellow crystalline residue. This residue was recrystallised from chloroform-light petroleum and then from dilute methanol, yielding colourless needles (0.5 g), m. p. 133—134°. $[\alpha]_D^{20}$ — 31° (chloroform, c = 3.0). The crystals are insoluble in 2 *N* sodium hydroxide and give no colour with ferric chloride in alcoholic solution or with diazotised benzidine. Reduction with magnesium-hydrochloric acid gives an orange colour.

$C_{17}H_{16}O_5$ (300.3)	Calc.	C	68.0	H	5.37	OCH_3	20.7
	Found	»	68.3	»	5.41	»	20.4

Methylation of pinobanksin with an excess of dimethyl sulphate

Pinobanksin (0.85 g) was dissolved in dry acetone (40 ml). To the solution were added dimethyl sulphate (1.0 ml = 3.5 moles) and freshly ignited potassium carbonate (5 g). The solution was boiled under reflux for 20 hours. The acetone was then evaporated on the steam bath, and the residue acidified with 2 *N* sulphuric acid and then taken up in ether (150 ml). The yellow ether solution was washed with 1 *N* sodium hydroxide (2 × 50 ml) to remove any monomethyl ether. It was then dried over anhydrous sodium sulphate and the solvent evaporated, leaving a yellow syrup, which slowly deposited crystals. After stirring with ether, the crystals could be separated by filtration. More crystals were obtained from the filtrate on standing. The crystals were collected and recrystallised twice from methanol. Yield, 0.05 g of a pale yellow crystalline powder, m. p. 197—198°. No m. p. depression was observed on admixture with galangin trimethyl ether *.

$C_{18}H_{18}O_5$ (314.3)	Calc.	C	68.8	H	5.77	OCH_3	29.6
$C_{18}H_{16}O_5$ (312.3)	Calc.	»	69.2	»	5.16	»	29.8
	Found	»	69.3	»	5.17	»	30.3

The formula $C_{18}H_{18}O_5$ corresponds to pinobanksin trimethyl ether and $C_{18}H_{16}O_5$ to galangin trimethyl ether.

Dehydrogenation of pinobanksin

Pinobanksin (0.5 g), cinnamic acid (1.2 g), palladium-charcoal catalyst prepared as described by Ott and Eichler [17] (0.25 g) and water (25 ml) were heated in a stainless-steel bomb rotating in an oil bath at 180° for one hour. After cooling, the reaction mixture

* A sample of this substance was kindly supplied by Prof. T. R. Seshadri, Delhi, India.

was extracted with ether (50 ml) and the cinnamic acid removed by shaking with saturated sodium bicarbonate solution (4 × 50 ml). The brownish ether solution was dried over anhydrous sodium sulphate and filtered through a column of aluminium oxide. The brown impurities were adsorbed, and the pale yellow filtrate yielded a bright yellow residue on concentration. It melted at 200—210°. After two recrystallisations from dilute methanol, the m. p. was raised to 215—216°. Yield, 0.15 g.

$C_{15}H_{10}O_5$ (270.2)	Calc.	C	66.7	H	3.73
	Found	»	66.8	»	3.80

As no sample of galangin was available, this flavonol was prepared by demethylation of its 5,7-dimethyl ether with pyridine hydrochloride at 180°, a method which has recently been successfully applied to methylated phenols [18]. The galangin thus obtained was purified by vacuum sublimation and recrystallisation from dilute methanol. It melted at 213—215° and gave no m. p. depression with the sample obtained from pinobanksin.

Dehydrogenation of pinobanksin dimethyl ether

Pinobanksin dimethyl ether was dehydrogenated in the same way as described for pinobanksin. A pale yellow product was obtained, forming fibrous crystals from methanol. M. p. 172—173°. The m. p. was not depressed on admixture with a synthetic sample of galangin 5,7-dimethyl ether, prepared according to Kostanecki, Lampe, and Tambor [19]. These authors found a m. p. of 177—178°, but the sample prepared by the present author melted at 173—174°.

$C_{17}H_{14}O_5$ (298.3)	Calc.	C	68.5	H	4.73	OCH_3	20.8
	Found	»	68.3	»	4.79	»	20.6

Rearrangement of pinobanksin dimethyl ether to "apoalpinone monomethyl ether"

Pinobanksin dimethyl ether (0.1 g) was dissolved in 10 ml of methanol, containing 1 g of potassium hydroxide. The solution was boiled under reflux for 10 minutes. The yellow solution was then cooled and acidified with 2 *N* sulphuric acid. The methanol was evaporated, and the resulting aqueous suspension extracted with ether. The ether solution, after drying and concentration, yielded a yellow crystalline residue, which turned almost colourless on washing with methanol and ether (m. p. 169—171°). After recrystallisation from dilute methanol and from chloroform-light petroleum, colourless needles, m. p. 170—171°, $[\alpha]_D^{20}$ zero, were obtained. Yield, 0.05 g.

The substance gives a yellow solution in cold 2 *N* sodium hydroxide but gives no colour reaction when reduced with magnesium-hydrochloric acid.

$C_{17}H_{16}O_5$ (300.3)	Calc.	C	68.0	H	5.37	OCH_3	20.7
	Found	»	67.5	»	5.33	»	20.3

The acetate was prepared by acetylation with acetic anhydride-pyridine. Colourless crystals from dilute methanol, m. p. 112—114°.

$C_{17}H_{15}O_4$ ($OOCCH_3$) (342.3)	Calc.	CH_3CO	12.6
	Found	»	12.8

Synthesis of "apoalpinone monomethyl ether"

2'-Hydroxy-4',6',α-trimethoxychalkone (VII) was first prepared by condensing 2-hydroxy-4,6,ω-trimethoxy-acetophenone (prepared according to Row and Seshadri [14]) with benzaldehyde as described by Kimura [13]. 1.5 g of the ketone yielded 1.4 g of the chalkone, m. p. 111—112° (Kimura 112°).

The chalkone (0.85 g) was boiled with ethanol (100 ml) and 2 *N* sulphuric acid (20 ml) for 24 hours under reflux. The ethanol was then evaporated on a steam bath. On cooling, the remaining aqueous solution deposited a colourless, sticky solid, which was extracted with ether. The ether solution was shaken with 1 *N* sodium hydroxide solution (2 × 20 ml), and the alkaline extract acidified. A colourless precipitate appeared, which was taken up in chloroform. The chloroform solution was dried and concentrated, leaving an almost colourless crystalline residue. After two recrystallisations from chloroform-light petroleum and one from dilute methanol, the m. p. was constant at 169—170°. Yield, 0.3 g. Mixed m. p. with the product obtained by alkali treatment of pinobanksin dimethyl ether 170—172°.

$C_{17}H_{16}O_5$ (300.3)	Calc.	C	68.0	H	5.37	OCH_3	20.7
	Found	»	67.3	»	5.46	»	20.3

The acetate melted at 112—113° and gave no m. p. depression when mixed with the acetate of rearranged pinobanksin dimethyl ether.

An attempt to dehydrogenate "apoalpinone monomethyl ether" with palladium-cinnamic acid yielded a yellowish brown sticky product along with unchanged starting material.

Ultraviolet light absorption

The ultraviolet light absorption of pinobanksin and its dimethyl ether was measured in absolute ethanol with a Beckman Spectrophotometer, Model DU.

SUMMARY

Pinobanksin, a common pine heartwood constituent, is 3,5,7-trihydroxyflavanone (dihydrogalangin). The tribenzoate, the 7-monomethyl ether and the 5,7-dimethyl ether of pinobanksin have been prepared. The structure has been proved by catalytic dehydrogenation of pinobanksin and its dimethyl ether to the corresponding galangin derivatives. An attempt to prepare pinobanksin trimethyl ether led to galangin trimethyl ether, due to dehydrogenation.

Pinobanksin dimethyl ether has been rearranged by alkali to an isomeric compound earlier described as 3-hydroxy-5,7-dimethoxyflavanone ("apoalpinone monomethyl ether"). This substance, however, does not give the colour reactions characteristic to flavanones and cannot be dehydrogenated to the corresponding galangin dimethyl ether.

The ultraviolet light absorption of pinobanksin and its dimethyl ether has been studied.

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